



⑫

## EUROPEAN PATENT SPECIFICATION

⑯ Date of publication of patent specification: 11.12.91 ⑮ Int. Cl. 5: C03C 8/02, C03C 10/08  
⑯ Application number: 88106600.5  
⑯ Date of filing: 25.04.88

⑤4 Ceramic coated metal substrates for electronic applications.

⑩ Priority: 04.05.87 US 45930  
⑩ Date of publication of application:  
09.11.88 Bulletin 88/45  
⑩ Publication of the grant of the patent:  
11.12.91 Bulletin 91/50  
⑩ Designated Contracting States:  
DE FR GB  
⑩ References cited:  
EP-A- 0 016 307  
EP-A- 0 080 346  
EP-A- 0 289 222

⑦3 Proprietor: ALLIED-SIGNAL INC. (a Delaware corporation)  
Columbia Road and Park Avenue P.O. Box 2245R  
Morristown New Jersey 07960(US)  
⑦2 Inventor: Oboodi, Reza M.  
c/o Allied-Signal Inc. P.O. Box 2245R  
Morristown, NJ 07960(US)  
Inventor: Blazej, Daniel C.  
c/o Allied-Signal Inc. P.O. Box 2245R  
Morristown, NJ 07960(US)  
⑦4 Representative: Brock, Peter William  
URQUHART-DYKES & LORD 91 Wimpole  
Street  
London W1M 8AH(GB)

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

EP 0 289 903 B1

## Description

This invention relates to ceramic coated metal substrates for use in electronic applications. More particularly, this invention relates to such coated substrates having improved processibility characteristics in the manufacture of electronic devices, as for example electronic circuits.

In the manufacture of electronic devices, it is standard to mount or form the various electronic components which comprise the circuits of the devices on a substrate. Various materials have been suggested for use as the substrate. For example, relatively large circuits such as those employed in radios, televisions, computers and the like are generally produced on organic substrates, as for example, reinforced thermosetting resins, reinforced phenolic resins and reinforced epoxy resin laminates.

The organic plastic circuit boards have some advantages. For example, such boards are relatively inexpensive, can be manufactured in almost any desired size with flat smooth surfaces and have reasonably good physical strength. Such organic plastic circuit boards also display a number of deficiencies which greatly limit their utility. For example, these materials are heat sensitive and cannot be exposed to high temperatures, i.e. temperatures in excess of 400 °C. Thus, metal circuitry and the like must be formed on the surface of the board using low temperature deposition. Moreover, organic plastic substrates cannot be used with newer methods of applying circuits to non-conductive substrates which are lower in cost and provide improved reliability and electrical accuracy but which demand firing temperatures in excess of 600 °C. Another disadvantage of plastic circuit boards is that resistors, capacitors, and the like must be manufactured as discrete components in separate manufacturing operations, and then individually mounted on the board. In addition to the wide variety of manufacturing processes required to make a low temperature circuit board, the use of discrete components severely limits the packing density which can be achieved.

The disadvantages of plastic circuit boards have led to the development of circuit manufacturing techniques which allow direct formation of components (conductors, resistors, capacitors, and the like) on the surface of the substrate, (see M. L. Topfer, "Thick-Film Microelectronics", Van Nostrand Reinhold, NY, 1971, and F.N. Sinnadurai, "Handbook of Microelectronics Packaging and Interconnection Technologies", Electrochemical Publications Limited, Great Britain, 1985). The materials used to form these so called process induced components (PIC) are usually prepared in the form of inks comprising metal or ceramic powders, glass powders, polymer binders, and a liquid carrier which are printed on the substrate and heated to drive off the organic binder and fuse the remaining components to the substrate. The firing temperatures required for this process typically range from 600 °C to 950 °C, considerably in excess of the degradation temperatures of any organic plastic circuit board. The components prepared at these high temperatures generally exhibit very good reliability and electrical accuracy in addition to being relatively low in cost.

Other circuit board substrates have been fabricated out of ceramic substrates. A variety of ceramic materials are commercially available for use as high temperature substrates. Most notable is aluminum oxide. Examples of such substrates are described in Kuzel, R. et al., "Ceramic-Coated Copper Substrates for Hybrid Circuits", Hybrid Circuits, No. 4, pp. 4-9 (1984). These substrates composed of aluminum oxide have the advantages that they have excellent high temperature resistance and may be fired and refired at high temperatures, for example, temperatures of from 600 °C to 900 °C. Substrates formed from aluminum oxide are relatively inexpensive when the wafers are small and of simple shape, and has therefore become something of an industry standard. However, these materials also suffer from several disadvantages. An inherent disadvantage of ceramic substrates is that they are quite fragile. This places a significant size limitation on their use and, oftentimes, special fixturing is required to prevent damage while in use. Another disadvantage of ceramic substrates is that they can be quite difficult and costly to machine. These aspects of ceramics generally limit their use to small, rectangular, single sided circuits which have very high reliability and precision.

Still other circuit boards have been fabricated out of porcelain coated metals such as steel and copper clad Invar. Illustrative of such materials are those described in U.S. Patent No. 4,256,796; Onyshkevych, L.S., et al., "Manufacturing Steps in the Production of Porcelain-Enamel PC Boards", RCA Review, Vol. 42, pp. 145-158 (1981); Nobuo, I., et al., "Thick Film Circuit on Bent Porcelain-Bent Substrate", Int. J. Hybrid Microelectron., 5(2), pp. 1 to 8 (1982); Hugh, S.C., "Multilayer Thick-Film Circuits on Porcelanized Steel Substrates", Int. J. Hybrid Microelectron., 4(2), pp. 326-330 (1981); Hang K.W., et al, "Low Expansion Porcelain-Coated Copper-Clad Invar Substrates", RCA Review, Vol. 45, pp. 33-48 (1984); Prabhu, A.N., et al., "Optimization of RCA Porcelain for Compatibility With Thick Films", RCA Review, Vol. 42, pp. 221 to 237 (1981); Hughes, E.W., "Status Report on Porcelain Enamelled Metal Substrates", Ceramic Eng. Soc. Proc. 5, p. 219-220 (1984); Schabacker, R.B., "The Multiplicity of Variations in PEMs", Appliance, 39(6), pp. 76-

79 (1982); Schelhorn, J.L., "Metal Core Materials for Thick Film Substrate Applications", Int. J. Hybrid Microelectron., 4(2), pp. 347-352 (1981); Hang, K.W., et al., "High-Temperature Porcelain-Coated-Steel Electronic Substrates-Composition and Properties, RCA Review, Vol. 42, pp. 159-177 (1981); and Onyshkevych, L.S., "Porcelain-Enameled Steel Substrates for Electronic Applications", Appliance, 38 (4), pp. 46-49 (1981). Although these boards are not subject to thermal degradation as the organic plastic boards, and are substantially stronger than ceramic, they do suffer from certain process and use deficiencies. For example, when low temperature porcelains are fired to the metal they melt and flow in such a way that a meniscus is formed at all edges. It therefore becomes very difficult to print circuitry over the resulting uneven surface. A further problem with low temperature porcelains is that they soften and reflow at about 10 600 °C which can lead to distortion of the overlying circuitry. Another problem with porcelains is poor adhesion to the metal substrate during use because of substantial differences between the coefficients of thermal expansion of the porcelain and the metal substrate.

Several attempts have been made to obviate the deficiencies of the porcelain-coated substrates. For example, U.S. Patent No. 4,258,798 discloses the fabrication of porcelain-coated metal circuit boards 15 wherein the porcelain is a devitrified glass, and U.S. Patent Nos. 4,358,541 and 4,385,127 describe essentially alkali metal free glass-ceramic coatings for use in the manufacture of circuit boards. While relatively effective these boards also suffer from several disadvantages. For example, the thermal coefficients of expansion (TCE) of the glass or devitrified glass when matched to the TCE of the metal core results in a substrate with TCE's which are not a good match for TCE's of surface mounted components. 20 For example, in the case of partially devitrified glass, the resultant fired coatings have deformation temperatures greater than 700 °C and thermal coefficients of expansion values greater than 11 ppm/°C. Although the high TCE is considered an advantage for adhesion to the metal core, it is a disadvantage when considering a good match to the surface mounted components (typically alumina or silicon) which have TCEs in the 6 to 8 ppm/°C range.

25 Ceramics containing aluminum oxide, silicon oxide and magnesium oxide are known. For example, cordierite-based glass ceramic materials are described in Mussler, B.H. and Shafer, M.W., "Preparation and Properties of Mullite-Cordierite Composites.", Ceramic Bulletin, Vol. 63, No. 5, pp. 705-714 - (1984), and references cited therein. As noted in Ceramic Bulletin, when compared to alumina, presently the most 30 commonly used material, cordierite ( $2\text{MgO}\cdot 2\text{Al}_2\text{O}_3\cdot 5\text{SiO}_2$ ) offers lower dielectric constant and thermal expansion, but has disadvantage of inferior mechanical properties. Because of the low thermal expansion and inferior mechanical properties of cordierite, it would be expected that the fabrication of electronic devices composed of metal substrates which have relatively high thermal coefficients of expansion coated with cordierite or cordierite based glass ceramic which have relatively low thermal coefficients of expansion would not be feasible because of the large differences in thermal coefficients of expansion.

35 This Invention relates to a ceramic coated article, having a metal core and having on at least a portion of the surface of the metal core a coating of a glass ceramic, based on its oxide content and on the total weight of the coating, comprising

- 40 (a) from 8 to 26 % by weight of magnesium oxide ( $\text{MgO}$ );
- (b) from 10 to 49 % by weight of aluminum oxide ( $\text{Al}_2\text{O}_3$ ) and;
- (c) from 42 to 68 % by weight of silicon oxide ( $\text{SiO}_2$ ).

Several advantages flow from the invention. For example, the ceramic/glasses used in this invention have a high temperature refiring capability (>850 °C), and are air firable. Moreover, the article of this invention exhibits a composite thermal coefficient of expansion which is optimum for use in electronic devices, and exhibits a low dielectric constant which allows for use with high frequency circuits and allows 45 for greater applicability in electronic applications. Furthermore the ceramic/glasses used in this invention exhibit strong adhesion to the metal substrate after firing and are very resistant to thermal stress. This avoids breakdown of the devices formed from the article of this invention when such articles are exposed to high temperatures normally encountered in the operation of electronic devices. This resistance to thermal stress is indeed surprising in view of the relatively large difference in the thermal coefficient of expansion of the metal substrate and the ceramic glass, and the prior teachings that the metal and coating coefficients of 50 expansion must be matched to produce good adhesion.

Lastly, the combination of relatively low TCE coating (TCE usually less than 4 ppm/°C) with the relatively high TCE metal (TCE usually 10 ppm/°C) produces a composite coated substrate having a TCE 55 within the preferred range (usually from 6 to 8 ppm/°C) which allows for a good TCE match between the substrate and surface mounted components which are usually alumina or silicon having TCE's in the range of from 6 to 8 ppm/°C.

Yet another aspect of this invention comprises a process for manufacturing a glass/ceramic coated article having a metal core and having on at least a portion of the surface of the metal core a coating of a

glass ceramic, said process comprising:

- (a) heating a metal substrate in the presence of oxygen at a first temperature for a time sufficient to form any amount of an oxide layer on the surfaces of said substrate;
- 5 (b) applying to all or a portion of the surfaces of said substrate a suspension comprising one or more organic solvents, one or more heat degradable polymeric binders and a calcined mixture of finely divided non-conductive materials comprising:
  - (i) from 8 to 26 % by weight of MgO;
  - (ii) from 10 to 49 % by weight of Al<sub>2</sub>O<sub>3</sub>; and
  - (iii) from 42 to 68 % by weight of SiO<sub>2</sub>;
- 10 (c) heating the coated/metal substrate combination of step (b) at a second temperature for a time sufficient to remove substantially all of said solvents from the applied suspension;
- (d) heating said coated/metal substrate combination of step (c) at a third temperature for a time sufficient to degrade substantially all of said binders in said applied suspension;
- 15 (e) heating the coated/metal substrate combination of step (d) at a fourth temperature for a time sufficient to sinter said non-conductive material to form a device comprising a metal substrate having a predetermined pattern of glass/ceramic material bonded to one or more surfaces thereof, said material comprising (on an oxide basis):
  - (i) from 8 to 26 % by weight of MgO;
  - (ii) from 10 to 49 % by weight of Al<sub>2</sub>O<sub>3</sub>; and
  - 20 (iii) from 42 to 68 % by weight of SiO<sub>2</sub>, and
- (f) heat treating said device at a fifth temperature for a time sufficient to recrystallize any residual glass contained in said material to any extent.

The process of this invention provides for greater selectivity in the application of the glass/ceramic materials to specific sites on a substrate which provides for greater freedom in the manufacture of devices. 25 After processing in accordance with this invention the coating contains crystallized glass/ceramic which is strongly adherent to the metal core and is suitable as a substrate for processed induced components.

Referring to the drawings:

- Fig. 1 is a perspective view of an embodiment of the ceramic coated substrate of this invention.
- Fig. 2 is an enlarged latitudinal sectional view of the substrate of Fig. 1 taken along line 2-2.
- 30 Fig. 3 is a perspective view of an embodiment of the ceramic coated substrate of this invention having an electrical circuit on the surface thereof.
- Fig. 4 is an enlarged latitudinal sectional view of the substrate of Fig. 3 taken along line 4-4.

Referring to Figs 1 and 2, a coated metal substrate in accordance with the present invention is indicated at 10. Substrate 10 includes a metal layer 12 having a number of through holes 14 for surface mounting other electronic components and for receipt of interconnecting devices for providing electrical connection between device 20 formed from substrate 10 and other electronic devices; substrate 10 also includes holes 28 for connecting the substrate to supporting structure (not depicted), and a non-conductive layer 16 composed of the ceramic glass of this invention heat bonded to selective portions of the top and/or bottom surfaces of metal substrate 12. In the preferred embodiments of the invention depicted to Figs. 1 and 2, 35 metal layer 12 consists of an elongated solid metal strip. Metal layer 12 is composed of a metal such as copper, nickel, cobalt, iron, aluminum and the like, metals, and alloys thereof which is resistant to oxidation when heated at high temperature in the presence of oxygen. Preferred for use in the practice of this invention are metals which can be exposed to temperatures in excess of 1100 °C in an oxidizing atmosphere without excessive spalling and which have thermal coefficients of expansion  $\geq 10 \text{ ppm/}^{\circ}\text{C}$ , preferably  $\geq 12 \text{ ppm/}^{\circ}\text{C}$  over the temperature range of from 50 °C to 250 °C. Illustrative of such preferred alloys are those alloys based on cobalt, nickel, and iron and which optionally include aluminum and which preferably also include chromium. Particularly preferred metals for use in the construction of metal layer 12 are nickel based alloys as for example, the nickel alloy HAYNES® alloy No. 214 available from Haynes Corporation and the iron based alloys, as for example, the iron based alloys Alfa-IVTM and Fecralloy 40 available from Allegheny Ludlum Steel Corporation.

In general, the thickness of layer 12 will vary from 0.025 mm to 0.75 mm. In the preferred embodiments of the invention, layer 12 is from 0.075 mm to 0.6 mm in thickness and in the particularly preferred embodiments is from 0.125 mm to 0.5 mm in thickness. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the thickness of layer 12 is from 0.2 mm to 0.4 mm.

55 Non-conductive layer 16 is bonded selectively to the bottom and top surfaces of metal substrate 12 to provide the desired effect. In this invention, layer 16 is composed of a ceramic/glass composition. In general, ceramic/glass coating 16 will include on an oxide basis based on the total weight of the coating of (a) from 8 to 26 % by weight of MgO; (b) from 10 to 49 % by weight of Al<sub>2</sub>O<sub>3</sub>; and (c) from 42 to 68% by

5 weight of  $\text{SiO}_2$ . In the preferred embodiments of the invention, useful ceramic-glass coatings will include on an oxide basis (a) from 9 to 22 % by weight of  $\text{MgO}$ ; (b) from 16 to 45 % by weight of  $\text{Al}_2\text{O}_3$ ; and (c) from 43 to 63 % by weight of  $\text{SiO}_2$ . In the particularly preferred embodiments of the invention, useful ceramic-glass coating will include on an oxide basis (a) from 10 to 18 % by weight of  $\text{MgO}$ ; (b) from 23 to 40 % by weight of  $\text{Al}_2\text{O}_3$ ; and (c) from 44 to 58 % by weight of  $\text{SiO}_2$ . Amongst these particularly preferred embodiments of the invention, most preferred are those embodiments in which useful ceramic-glass coating includes (a) from 12 to 14 % by weight of  $\text{MgO}$ ; (b) from 30 to 35 % by weight of  $\text{Al}_2\text{O}_3$ ; and (c) from 45 to 52 % by weight of  $\text{SiO}_2$ .

10 The glass/ceramic for use in this invention may be any one of the glass/ceramics based on ternary metal oxide systems containing varying amounts of the three components,  $\text{MgO}$ ,  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . Illustrative of useful ternary metal oxide systems are cordierite ( $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ ), sapphirine ( $4\text{MgO}-5\text{Al}_2\text{O}_3-2\text{SiO}_2$ ) and the like. In the preferred embodiments of the invention, the glass/ceramic coating will contain varying amounts of cordierite ( $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ ) but in addition may include sapphirine ( $4\text{MgO}-5\text{Al}_2\text{O}_3-2\text{SiO}_2$ ).

15 In the preferred embodiments of this the ceramic coating also includes (on an oxide basis) boron oxide and one more alkali metal or alkaline earth metal oxides, preferably an alkali metal oxide such as  $\text{Li}_2\text{O}$ ,  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  and more preferably  $\text{Li}_2\text{O}$ . These preferred oxide components are derived from "fluxing and sintering agents" added to the glass/ceramic during its manufacture. In the preferred embodiments of the invention, the amount of alkali metal or alkaline earth metal oxides is from 1 to 4 weight percent based on the total weight of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the composition and the amount of boron oxide is from 3 to 13 weight percent on the aforementioned basis. In the particularly preferred embodiments of the invention, the amount of the alkali metal or alkaline earth metal oxides is from 1 to 3 weight percent, and the amount of boron oxide is from 4 to 10 weight percent. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the amount of alkali metal or alkaline earth metal oxide is from 2 to 3 weight percent, and the amount of boron oxide is from 5 to 7 weight percent.

20 25 The glass/ceramic coating may also optionally include from 0 to 11% by weight based on the total weight of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the composition of one or more oxides which function as nucleating agents. Illustrative of such agents are transition metal oxides, such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$ ,  $\text{La}_2\text{O}_3$  and the like. Preferred nucleating agents are  $\text{TiO}_2$  and  $\text{ZrO}_2$ , and the most preferred nucleating agent is  $\text{TiO}_2$ . In the preferred embodiments of the invention, the amount of the nucleating agent is from 2 to 8 weight percent, based on the total weight of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the composition, and in the particularly preferred embodiments of the invention, the amount of the nucleating agents is from 4 to 8 weight percent on the aforementioned basis.

30 35 An especially preferred coating contains cordierite ( $2\text{MgO}-2\text{Al}_2\text{O}_3-5\text{SiO}_2$ ) and spodumene ( $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-4\text{SiO}_2$ ), and optionally  $\text{TiO}_2$  and/or sapphirine ( $4\text{MgO}-5\text{Al}_2\text{O}_3-2\text{SiO}_2$ ). These coatings are characterized as having thermal coefficients of expansion of from 1.9 to 2.5 ppm/ $^{\circ}\text{C}$  over a temperature range of from 50  $^{\circ}\text{C}$  to 250  $^{\circ}\text{C}$ .

40 The thickness of non-conductive layer 16 can vary widely. In general, layer 16 is from 0.020 mm to 0.100 mm in thickness. In the preferred embodiments of this invention, the thickness of layer 16 is from 0.025 mm to 0.085 mm, and in the particularly preferred embodiments is from 0.030 mm to 0.070 mm. Amongst these particularly preferred embodiments of the invention, the thickness of layer 16 is from 0.040 mm to 0.060 mm.

45 As depicted in electronic device 20 of Fig. 3 and Fig. 4, a conductive circuit pattern 18 is optionally applied selectively to the top and bottom surfaces of layer 16 in such a manner us to obtain the desired electronic effect. In the preferred embodiments of this invention as depicted in these Figures, conductive layer 18 consists of finely divided metal which has been sintered and heat bonded to the surface of non-conductive layer 16, in a desired circuit pattern. The type of metal which can be used in the construction of pattern 18 can vary widely, and can be any type of metal normally used in the formation of electrical circuits. Illustrative of useful metals are copper, nickel, palladium, platinum, silver, aluminum, gold and the like, and alloys thereof.

50 55 Thickness of pattern 18 can vary widely. Usually layer 18 has a thickness of from 0.005 to 0.075 mm. In the preferred embodiments of the invention, the thickness of layer 18 is from 0.01 to 0.06 mm, and in the particularly preferred embodiments is from 0.015 to 0.05 mm. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the thickness of layer 18 is from 0.02 to 0.03 mm.

60 65 Various other components are included in the electronic device 20 depicted in Fig. 4. For example, the device includes a resistor 22 bonded to the surface of non-conductive layer 16 between two conductive paths 18. Resistor 22 can be composed of any material commonly used to form resistors, or for example, ruthenium oxide. The electronic device of Fig. 4 also includes a capacity element 24, which is a sandwich

structure comprising overlapping conductive patterns 18(a) and 18(b) bonded to and sandwiching a layer 26 which is composed of finely divided dielectric material such as one or more ferroelectric materials, for example, barium titanate, lead magnesium niobate, strontium titanate, lead titanate, calcium titanate, calcium stannate, lead magnesium tungstate, barium potassium titanium niobate, calcium zirconate and sodium tantalate, either alone or in combination with one or more glasses such as silicate, borate and germanate glasses. Capacity element 24 can be formed by heat sintering and bonding finely divided materials by very substantially the same techniques used to form layer 16 and conductive pattern 18 discussed below.

The ceramic coated substrate and the electronic circuit of this invention can be manufactured through use of the process of this invention. In the first step of the process of this invention, if required, metal substrate 12 of a desired configuration is treated to remove burrs, sharp edges, and the like to facilitate later coating with the ceramic. In the preferred embodiments of the invention, the metal substrate 12 is cleaned and degreased to remove foreign materials from the surface of substrate 12. Often metal substrates contain surface inhomogeneities which manifest themselves as pits in subsequent process steps. In the preferred embodiments of the invention, the metal surface is treated to remove such surface inhomogeneities. Amongst the several techniques available for accomplishing this task, preferred are polishing for example with sand paper, chemical etching and sand blasting. Metal substrate 12 is then heated in the presence of an oxidizing atmosphere, preferably air, at a first temperature for a time sufficient to form any amount of a metal oxide layer on one or more surfaces of said layer. The heat treatment of the metal is critical for the formation of an adherent oxide layer which forms a bonding interface for the deposited ceramic coating. The oxide layer so formed is preferably substantially homogeneous in order to prevent localized pitting or spalling. The temperature employed and the duration of the heating step will vary widely depending on the type of metal. In the preferred embodiments of the invention, metal substrate 12 is heated at a temperature of from 800 °C to 1250 °C for a period of from 1/2 to 24 hours, and in the particularly preferred embodiments, the metal substrate is heated at a temperature of from 1060 °C to 1200 °C for a period of from 1 to 12 hours. Amongst the particularly preferred embodiments of the invention, most preferred are those embodiments in which the metal substrate is heated to a temperature of from 1120 °C to 1180 °C for a period of 1 to 4 hours.

The method employed for heating metal substrate 12 is not critical and any conventional method can be used. For example, one convenient method is to heat the metal substrate at an appropriate temperature for an appropriate period of time in a box furnace which allows some air to pass in and out.

In the second step of the process of this invention a suspension comprising one or more organic solvents, one or more heat degradable polymeric binders and a calcined mixture of finely divided glass/ceramic comprising (on an oxide basis):

from 8 to 26% by weight of MgO  
from 10 to 49% by weight of Al<sub>2</sub>O<sub>3</sub>; and  
from 42 to 68% by weight of SiO<sub>2</sub>, is

applied to one or more surfaces of a metal. The types of non-conductive materials employed in the practice of this invention are as described above. The non-conductive materials are used in the form of finely divided particles. In the preferred embodiments of the invention, the materials are in the form of finely divided spherical or substantially spherical particles having an average diameter of not more than 10 micrometers, and in the particularly preferred embodiments such materials are in the form of finely divided spherical or substantially spherical particles having an average diameter of less than 5 micrometers. Amongst these particularly preferred embodiments most preferred are those embodiments in which non-conductive materials are in the form of finely divided spherical or substantially spherical particles in which the average particle diameter is less than 2 micrometers.

"Thermally degradable polymeric organic binders" are one component of the suspension which is applied to the substrate in step two. As used herein "thermally degradable polymeric organic binders" are naturally occurring or synthetic polymers which degrade when subjected to heat. Useful thermally degradable polymeric organic binders for use in this invention are also not critical and can also vary widely. Organic polymer binders for use in the practice of this invention preferably are capable of providing a stable colloidal suspension with the one or more non-conducting materials and one or more organic solvents, and is preferably thermally degradable when heated at temperature of at least 300 °C, and most preferably at a temperature from 300 °C to 600 °C to leave a substantially uniform sintered coating of the finely divided non-conductive material bonded to one or more surfaces of the metal. Polymers which do not substantially completely thermally degrade or which leave decomposition products which interfere with the capacitive capability of the capacitor are not preferred for use. In general, any naturally occurring or synthetic polymeric or elastomeric material can be used. Illustrative of such useful polymers are  $\alpha, \beta$ -unsaturated olefins such as polyvinyl alcohol, polyacrylates, polypropylene, polymethacrylates, polyvinyl chloride,

polyethylene, and the like; polyethers; polyesters such as polyethylene terephthalate, polybutylene terephthalate and the like; polyamides such as nylon-11, nylon-12, nylon-6, nylon-66 and the like; polysulfones; polyphenylene oxides; cellulose based polymers, such as methyl cellulose ethers, ethylpropyl cellulose ethers and hydroxypropyl cellulose ethers; and the like.

5 Another component of the suspension applied to the substrate in step two is one or more organic solvents. Organic solvents used to form the suspensions are not critical, and can vary widely. The only requirement is that the solvents are capable of dissolving the thermally degradable polymeric organic binders and capable of dispersing the one or more finely divided non-conductive materials so as to form a colloidal suspension or dispersion. In the preferred embodiments of the invention, organic solvents are  
10 those which volatilize when heated to a temperature of from 50 °C to 250 °C at atmospheric pressure, and in the particularly preferred embodiments organic solvents are those which volatilize when heated to a temperature of from 75 °C to 150 °C at atmospheric pressure. Amongst these particularly preferred embodiments most preferred are those organic solvents which volatilize when heated to a temperature of from 90 °C to 120 °C at atmospheric pressure. Illustrative of useful solvents are alcohols, esters, ketones,  
15 aldehydes, hydrocarbons and like organic solvents.

The last component of the suspension applied to the substrate in step two is a mixture of calcined glass/ceramics. The calcined glass/ceramic mixture is formed by forming a mixture of finely divided  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{MgO}$  in the above-referenced proportions, together with one or more "effective fluxing and sintering agents" and optionally one or more "effective nucleating agents". As used herein, "effective fluxing and sintering agents" are fluxing and sintering agents which are effective to increase the adhesion of the ceramic glass to the metal substrate to any extent. These agents are precursor materials for the alkaline earth metal and/or alkali metal oxides, or boron oxide contained in the coating. Illustrative of effective fluxing and sintering agents are alkali metal salts such as  $\text{LiBO}_2$ ,  $\text{Li}_2\text{O}$ ,  $\text{B}_2\text{O}_3$ ,  $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{Na}_2\text{O}$ ,  $\text{NaBO}_2$ ,  $\text{Li}_4\text{B}_6\text{O}_{11}$ ,  $\text{K}_2\text{O}$ ,  $\text{CaO}$ ,  $\text{LiF}$ ,  $\text{NaF}$ ,  $\text{LiCl}$ ,  $\text{NaCl}$ ,  $\text{Na}_2\text{SiF}_6$ ,  $\text{Na}_2\text{B}_4\text{O}_7$ ,  $4\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{LiAlSi}_3\text{O}_8$ ,  $\text{Li}_2\text{Si}_2\text{O}_5$ ,  $\text{BaB}_2\text{O}_4$ , and  
20 the like. Preferred effective fluxing and sintering agents are alkali metal borates, meta-borates, and like borates such as  $\text{LiBO}_2$ ,  $\text{Li}_2\text{B}_4\text{O}_7$ ,  $\text{Li}_2\text{Si}_2\text{O}_5$ ,  $\text{LiF}$ ,  $\text{BaB}_2\text{O}_4$ ,  $4\text{CaO} \cdot 5\text{B}_2\text{O}_3 \cdot 9\text{H}_2\text{O}$ . Particularly preferred effective fluxing and sintering agents are lithium borates and metaborates. Amongst these particularly preferred effective fluxing and sintering agents are  $\text{LiBO}_2$ ,  $\text{Li}_2\text{B}_4\text{O}_7$ , and  $\text{LiF}$ .

25 The amount of fluxing and sintering agents can vary widely. The amount of fluxing and sintering agents will depend on the amount of alkaline earth and/or alkali metal oxides, and boron oxides desired in the glass/ceramic composition. In general, the amount of such agents is from 1 to 15% based on the total weight of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the composition. In the preferred embodiments of the invention, the amount of fluxing and sintering agents is from 5 to 12 weight percent based on the total weight of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the composition, and in the particularly preferred embodiments of the invention the amount of fluxing and sintering agents is from 7 to 9 on the aforementioned basis.

30 As used herein, "effective nucleating agents" are nucleating agents which promote the crystallization of residual glass phases. Illustrative of such nucleating agents are metal oxides such as  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Y}_2\text{O}_3$ ,  $\text{Ta}_2\text{O}_5$  and  $\text{La}_2\text{O}_3$ . Preferred nucleating agents are  $\text{TiO}_2$  and  $\text{ZrO}_2$ , and a particularly preferred nucleating agent is  $\text{TiO}_2$ .

35 The effective nucleating agents are optional, and when used, the amount may vary widely. In general, the amount of such agents can vary from 0 to 11% by weight based on the total weight of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{SiO}_2$  in the composition. In the preferred embodiments of the invention, the amount of effective nucleating agents is from 2 to 8 weight percent based on the total weight of  $\text{MgO}$ ,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  in the composition, and in the particularly preferred embodiments of the invention, the amount of effective nucleating agents is  
40 from 4 to 6 weight percent based on aforementioned basis.

45 Preparation of the calcined glass/ceramic mixture involves well known procedures. The raw materials are weighed and combined according to the desired proportions. The raw materials can be added as pure oxides, or alternatively, in equivalent forms containing volatile species which are eliminated during subsequent heating. For example, magnesium carbonate can be used in place of magnesium oxide, or boric acid can be used in place of boron oxide. Similarly, the lithium oxide and boron oxide can be conveniently added in a precombined form such as  $\text{LiBO}_2$  or  $\text{Li}_2\text{B}_4\text{O}_7$ . The raw materials are thoroughly mixed, typically by wet milling in a ball mill with added solvent, such as isopropanol in an amount sufficient to form a slurry of the desired proportion of ingredients.

50 After filtering and drying to form a powder, the materials are calcined in order to produce the desired glass/ceramic composition. Calcination may be carried out using conventional procedures. For example, this process may be carried out in a box furnace with a slow heat up to allow for removal of any residual volatiles. Peak temperatures may vary, typically being in the range from 1100 °C to 1300 °C, and time at peak temperature may also vary, typically ranging from 2 to 20 hours. The resultant product is then

pulverized and ball milled in an appropriate solvent such as isopropanol using standard ceramic processing equipment to produce particles nominally less than 10 micrometers in diameter. This slurry is then filtered and dried to produce the fine powder which will subsequently be applied to a metal core together with one or more binders and organic solvents.

5 The amounts of the various ingredients in the suspension employed in the first step of the process of this invention can vary widely. Very dilute suspensions can be made for electrophoretic deposition and more concentrated suspensions for spraying, roller coating and the like. The preferred method in accordance with this invention is to make a high viscosity paste which is deposited in a screen printing process. The paste can be made with a variety of materials typical in the thick film industry. An illustrative 10 formulation is a mixture of 65 weight percent ceramic powder combined with an organic vehicle containing ethyl cellulose dissolved in a high molecular weight alcohol. In general, the lower the concentration of suspended non-conductive materials in the suspension the more often the suspension must be applied to the metal to provide a given thickness of such bonded/sintered non-conductive material in the final glass-ceramic coated substrate; and conversely, the higher the concentration of suspended non-conductive 15 materials in the suspension, the less often the suspension must be applied to the metal to provide a given thickness of bonded/sintered non-conductive material in the glass-ceramic coated substrate. In general, the concentration of organic solvents in the suspension will vary from 5 to 50 weight percent, the concentration of the non-conductive materials in the suspension will vary from 40 to 85 weight percent, and the concentration of polymeric binders in the suspension will vary from 1 to 15 weight percent based on the 20 total weight of the suspension. In the preferred embodiments of the invention, the concentration of organic solvents in the suspension will vary from 10 to 45 weight percent, the concentration of non-conductive materials in the suspension will vary from 45 to 80 weight percent, and the concentration of polymeric binders in the suspension will vary from 1 to 10 weight percent. In the particularly preferred embodiments, the concentration of organic solvents in the suspension is from 20 to 40 weight percent, the concentration of 25 non-conductive materials in the suspension is from 50 to 75 weight percent and the concentration of polymeric binders in the suspension is from 1 to 5 weight percent. All weight percentages are based on the total weight of the suspension.

The suspension is applied to one or more surfaces of the metal in a predetermined pattern. The suspension can be applied over all of the surfaces or over a portion thereof. Any suitable technique useful 30 for applying a suspension to the surface of a solid material can be used. Illustrative of useful techniques are screen printing, pad printing, dipping, spraying and the like. Such techniques of applying suspensions to a substrate are well known in the art and will not be described herein in great detail. Application by use of screen printing is preferred in accordance with this invention because of the ease with which patterns can be generated which allow open areas for mounting holes, ground plane interconnects, and electrically 35 isolated vias from one side to the other. Typically, the pattern is printed on both sides of the metal in order to maintain uniform stress and eliminate bowing.

The suspension can be applied in a single application or multiple applications can be made depending on the desired thickness of the layer of non-conductive material in the finished product. In the preferred 40 embodiments there are from 1 to 8 printed layers depending on the desired thickness and in the most preferred embodiments of the invention only 2 to 3 layers. In some instances it is preferred that the final top layer ceramic composition differ from the underlying layer or layers. In this way one can take advantage of those ceramic compositions with superior adhesive properties for direct contact to the metal core and those compositions with superior electrical properties for contact with the overlying circuitry.

The amount of the suspension applied to the metal at any particular situs will vary widely depending on 45 the desired thickness of the non-conductive material in the final glass-ceramic coated substrate. The amount of the suspension applied to the metal is sufficient, usually, to provide a layer of sintered non-conductive material bonded to the metal of a thickness of at least 20 micrometers. In the preferred embodiments of the invention, the amount applied is sufficient to provide a layer of non-conductive material having a thickness of from 25 to 85 micrometers, and in the particularly preferred embodiments, the amount 50 applied is sufficient to provide a layer of non-conductive material having a thickness of from 30 to 70 micrometers. Amongst these particularly preferred embodiments of this invention, most preferred are those embodiments in which the amount of suspension applied to the metal is sufficient to provide a layer of sintered non-conductive material bonded to the metal having a thickness of from 40 to 60 micrometers.

In the third step of the process of this invention, the metal to which the suspension has been applied in 55 the desired predetermined pattern and in the desired amount heated at a temperature and for a time sufficient to remove substantially all of the organic solvent from the applied suspension and to sinter the non-conductive material, and to bond the sintered material to the metal substrate or substrates as the case may be and to crystallize the residual glassy phase of the non-conductive material. The firing procedure is

important in that it determines the degree of adhesion and structure of the ceramic coating. The article is preferably placed at room temperature in a furnace which is subsequently programmed for a given temperature and time profile. In the preferred embodiments of the invention, the heating step is divided into two portions and has at least two plateaus. In these preferred embodiments, the metal substrate to which the suspension has been applied is first heated to a temperature sufficient to volatilize the solvents from the suspension, preferably in less than one hour without disturbing the integrity of the remaining composition to form a coating of a composition containing essentially no solvent and which comprises the finely divided non-conductive material and the binders coated on the surface of the substrate in the predetermined pattern. The purpose of this step is to ensure complete volatilization of the polymer binder so that preferably substantially no carbon containing residual is present. The heating step can be carried out in an air atmosphere, or in an atmosphere of non-oxidizing gas. Obviously, this heating temperature can vary widely depending on the volatilization temperature of the particular solvent or solvents employed. Usually, however, the heating step is carried out at a temperature equal to or less than 200 °C for a period equal to or less than 4 hours. In the preferred embodiments using preferred solvents, this heating step is carried out at a temperature of from 50 °C to 200 °C at atmospheric pressure for a period equal to or less than 2 hours, and in the particularly preferred embodiments of the invention using particularly preferred solvents, at a temperature of from 75 °C to 150 °C at atmospheric pressure for a period equal to or less than 1 hour. In the most preferred embodiments of the invention employing most preferred solvents, the first part of the heating step is carried out at a temperature of from 90 °C to 120 °C at atmospheric pressure for a period equal to or less than 0.5 hour.

In the second step of the split heating procedure the metal and coated composition from which the solvents have been substantially removed are heated at a temperature and for a time sufficient to degrade substantially all of the polymer organic binders in the composition and sinter the finely divided non-conductive material and bond same to one or more surfaces of the metal as the case may be, to produce a substantially uniform coating of finely divided non-conductive material on one or more surfaces of the metal. The heating temperature employed in the second part of the split heating step can vary widely and will depend on the particular polymer binders, non-conductive materials and metals employed and the temperature employed in the substrate heating step.

Polymer degrading and sintering can be carried out in a single step or in multiple steps. Preferably, polymer degrading and sintering are carried in two steps. In the first step the polymer is degraded. In this step the coated substrate from which solvent has been removed is heated at a temperature and for a time sufficient to degrade the polymer. Usually, this heating step is carried out at a temperature equal to or greater than 200 °C for a period equal to or less than 4 hours. In the preferred embodiments using preferred polymers, the polymer degrading step is carried out at a temperature of from 200 °C to 800 °C for a period equal to less or less than 2 hours and in the particularly preferred embodiments using particularly preferred polymers is carried out at a temperature of from 300 to 700 °C for a period equal to or less than about 1 hour. In the most preferred embodiments of the invention, employing most preferred polymers, the polymer degrading heating step is carried out at a temperature of from 400 °C to 600 °C for a period equal to or less than 0.5 hour.

After the polymer has been degraded to the desired extent, the coated substrate is then heated at a temperature and for a time sufficient to sinter the finely-divided non-conductive material and bond same to the surface of the metal substrate. In general, the coated substrate is heated at a temperature below the melting point of the metal of the substrate for a period equal to or less than 2 hours to sinter and bond the non-conductive material to the substrate. In the preferred embodiments of the invention, the coated substrate is heated at a temperature from 1000 °C to 1220 °C for a period equal to or less than 1 hour, and in the particularly preferred embodiments of the invention the coated substrate is heated at a temperature of from 1060 °C to 1200 °C for a period equal to or less than 0.5 hour. Amongst these particularly preferred embodiments, most preferred are those embodiments in which the coated substrate is heated at a temperature of from 1120 °C to 1180 °C for a period equal to or less than 10 minutes. Subsequent cool down is not critical and the natural cooling rate of the unpowered furnace is generally adequate.

During the solvent removal, sintering and polymer degrading steps, densification and some vitrification of the glass/ceramic may occur. This residual glass structure is not desirable and can be substantially eliminated by a final heat treatment. In this heat treatment step, the coated metal substrate is heated to a temperature and for a time sufficient to crystallize the residual glassy phase to the desired extent. Heating temperatures and times may vary widely depending on the nature of the components of the coating. This procedure can be carried out in a single step or in multiple steps. In the preferred embodiment of the invention, the procedure is carried out in two steps. In the first step, the coated metal substrate is usually heated to a temperature of from 600 °C to 900 °C for a period equal to or less than 1 hour. In the preferred

embodiments of the invention, the substrate is heated to a temperature from 650 °C to 850 °C for a period equal to or less than 0.5 hour, and in the most preferred embodiments of the invention, the coated substrate is heated for a period equal to or less than 15 minutes at a temperature of from 700 °C to 800 °C. In the second step of this split heating step, the coated substrate is heated at a temperature of from 800 °C to 1100 °C over a period of from 1 to 6 hours. In the preferred embodiments of the invention, the heating temperature is from 800 °C to 1050 °C and the heating period is from 1 to 6 hours; and in the particularly preferred embodiments of the invention, heating temperatures are from 850 °C to 1000 °C and heating times are from 1 to 4 hours. Amongst these particularly preferred embodiments of this invention, most preferred are those embodiments in which heating temperatures of from 900 °C to 950 °C and heating times of from 1 to 3 hours are employed.

The substrate so formed can be used to form electronic substrates. For example, a suspension of a finely divided metal, as for example, the metal used as the solid metal substrate, such as copper, silver, gold, aluminum, palladium, platinum and the like and alloys thereof, and containing one or more organic solvents having one or more polymeric binders dissolved therein, is applied to surface of the sintered and bonded non-conductive material. The combination is thereafter heated to volatilize substantially all of the solvents from the suspension and to degrade substantially all of the binders, thereby sintering the finely divided metal and bonding said sintered metal to the surface of the non-conductive material. The suspension can be applied to one or more surfaces of sintered and bonded non-conductive material in a predetermined pattern. The suspension can be applied over all of the surfaces or a portion thereof using the same techniques employed in the suspension application step 1. The suspension can be applied in a single application or multiple applications can be made depending on the desired thickness of the layer of metal in the finished electronic device. The components and the relative amounts of the components of the suspension are as used in the suspension of step 1.

In an alternative embodiment of the process of this invention, the combination of the metal and coated composition are used directly in the third step of the process. In this procedure, the thermal degradation of the binders, and the sintering and heat bonding of both the sintered non-conductive layer and the sintered metal layer are accomplished in a single high temperature second part of the split heating step.

The solvent volatilization, polymer degradation, and sintering procedures used in this step are essentially the same as used in step two of the process of this invention in heating the suspension of the non-conductive material to remove the solvents, degrading the polymer kinds, and sintering and bonding the resulting composition to the surface of the solid conductive material. As in the case of the earlier heating step 2, the heating step of this procedure is preferably carried out in two stages. In the first stage of the heating procedure, the applied suspension is heated to a temperature and for a time which is sufficient to volatilize the one or more solvents from the applied suspension. In the second stage of the heating procedure, the substrate coated with the dried suspension is heated at a temperature and for a time which is sufficient to sinter the finely divided metal, and bond the sintered metal to the surface of the non-conductive layer. In the case of the alternative embodiment of the process of this invention, the coated substrate is also heated to a temperature and for a time sufficient to sinter the finely divided non-conductive material and bond the material to the surface of the metal substrate. Usually in the case of the alternative embodiment, the coating of the finely divided metal and the coating of the non-conductive material are sintered and bonded using substantially the same heating conditions.

The thickness of the conductive layer is not critical and can vary widely. Usually, the layer has a thickness of from 0.005 to 0.075 mm. In the preferred embodiments of the invention, the conductive layer has a thickness of from 0.01 to 0.06 mm, and in the particularly preferred embodiments of the invention has a thickness of from 0.015 to 0.05 mm. Amongst these particularly preferred embodiments most preferred are those embodiments in which the conductive layer has a thickness of from 0.02 to 0.03 mm.

The process of this invention can be used to manufacture electronic devices of this invention. Such devices vary widely and include circuit board, capacitors and the like. The process is preferred for use in the manufacture of circuit board.

50 The following specific examples are present to more particularly illustrate the invention.

#### EXAMPLES 1 TO 18

##### General Procedure:

55

A mixture of MgO, Al<sub>2</sub>O<sub>3</sub>, and SiO<sub>2</sub>, close to stoichiometric ratio of 2:2:5 (cordierite) and about 4-10 wt% of Li<sub>2</sub>O, B<sub>2</sub>O<sub>3</sub> and/or Li<sub>2</sub>O, 2 B<sub>2</sub>O<sub>3</sub> with 0-10 wt% TiO<sub>2</sub> or ZrO<sub>2</sub> is ball milled in isopropanol to insure proper mixing and melt homogeneity. The slurry is then filtered, dried and calcined at 1100-1300 °C for 4-

12 hours. The solid product is then pulverized to form the compositions set forth in the following Table I.

TABLE I

5

|    | Composition<br>No. | Weight % |                                |                  |                   |                               |                  |
|----|--------------------|----------|--------------------------------|------------------|-------------------|-------------------------------|------------------|
|    |                    | MgO      | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Li <sub>2</sub> O | B <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> |
| 10 | 1                  | 12.5     | 31.7                           | 46.7             | 2.7               | 6.3                           | 0.0              |
|    | 2                  | 12.4     | 31.4                           | 46.2             | 3.0               | 7.0                           | 0.0              |
|    | 3                  | 12.5     | 31.7                           | 46.7             | 1.6               | 7.4                           | 0.0              |
|    | 4                  | 12.4     | 31.4                           | 46.2             | 1.8               | 8.2                           | 0.0              |
|    | 5                  | 11.7     | 29.6                           | 43.7             | 2.7               | 12.3                          | 0.0              |
|    | 6                  | 12.5     | 32.0                           | 47.0             | 2.6               | 5.9                           | 0.0              |
| 15 | 7                  | 9.7      | 47.8                           | 36.2             | 2.0               | 4.5                           | 0.0              |
|    | 8                  | 22.7     | 20.0                           | 45.4             | 2.4               | 5.5                           | 4.0              |
|    | 9                  | 12.0     | 30.5                           | 45.0             | 2.4               | 5.6                           | 4.5              |
|    | 10                 | 12.3     | 31.2                           | 45.9             | 1.8               | 4.2                           | 4.6              |
|    | 11                 | 22.7     | 19.1                           | 45.2             | 2.4               | 5.6                           | 5.0              |
|    | 12                 | 11.2     | 28.3                           | 41.7             | 2.5               | 5.8                           | 10.5             |

The pulverized product can be blended with a suitable organic vehicle to form a printable paste.

The substrate is a nickel alloy (214 Haynes Corporation). The surface of this alloy is first chemically etched for at least 30 minutes for initial oxide removal, followed by heat treatment at a temperature at which the final product (coated substrate) is fired. This step provides an oxide layer which enhances the bonding between the metal and coating. This also prevents diffusion of metal into the coating, causing discoloration. After surface preparation, the metal is coated with the ceramic paste via screen printing. The printed substrates are allowed to settle at room temperature for 15-20 minutes followed by drying at 120°C for 30-45 minutes. The dried samples are then fired in air at 1140-1300°C for 1-15 minutes. The fired products can either be quenched at room temperature or allowed to cool slowly at the furnace cooling rate (ca. 40°C/minute). The final step in this process is heat treatment of the final products at 750-1000°C for 2-24 hours to crystallize the residual glassy phase. The following Table II sets forth the processes and materials which produce good adhesion between the ceramic and metal.

35

40

45

50

55

TABLE 2

| 5  | <u>Example No.</u> | <u>Metal Preparation</u>                 | <u>Heat Treatment in Air</u> |
|----|--------------------|--|------------------------------|
|    |                    | <u>Initial Oxide Removal</u>             | <u>(Temp/Time)</u>           |
| 10 | 1                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
|    | 2                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
|    | 3                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
|    | 4                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
|    | 5                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
|    | 6                  | FeCl <sub>3</sub> /HCl Etch              | 800°C/30 min                 |
| 15 | 7                  | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 8                  | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 9                  | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 10                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 11                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
| 20 | 12                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 13                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 14                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 15                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
|    | 16                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1200°C/30 min                |
| 25 | 17                 | H <sub>2</sub> SO <sub>4</sub> /HCl Etch | 1220°C/15 min                |
|    | 18                 | Sand, 400 grit                           | 1150°C/8 hrs                 |

30

TABLE 2 (Continued)

| 35 | <u>Example No.</u> | <u>Ceramic Formulation</u> | <u>Firing Process</u> |
|----|--------------------|----------------------------|-----------------------|
|    |                    | <u>Peak Temp °C</u>        | <u>Time (min)</u>     |
| 40 | 1                  | 1                          | 1150 20               |
|    | 2                  | 1                          | 1300 1                |
|    | 3                  | 2                          | 1300 1                |
|    | 4                  | 3                          | 1300 1                |
|    | 5                  | 4                          | 1300 1                |
|    | 6                  | 5                          | 1150 1                |
|    | 7                  | 7                          | 1250 2                |
|    | 8                  | 7                          | 1275 2                |
| 45 | 9                  | 8                          | 1200 2                |
|    | 10                 | 8                          | 1225 2                |
|    | 11                 | 8                          | 1250 2                |
|    | 12                 | 9                          | 1200 2                |
|    | 13                 | 9                          | 1225 2                |
| 50 | 14                 | 9                          | 1250 2                |
|    | 15                 | 10                         | 1225 2                |
|    | 16                 | 12                         | 1200 2                |
|    | 17                 | 11                         | 1175 2                |
|    | 18                 | 9                          | 1160 10               |

55

Example 19

Aggalloy was degreased and heat treated in air for 45 minutes at  $1200^{\circ}\text{C}$  to build up an oxide layer. The metal was then printed with a paste containing dielectric composition 9, dried, fired at  $1175^{\circ}\text{C}$  for three minutes, and then heat treated at  $900^{\circ}\text{C}$  for two hours. The resultant ceramic had very good adhesion to the metal.

5

#### Example 20

The identical dielectric and process procedure of Example 19 was used with Fecralloy as the supporting metal. Again, there was very good adhesion of ceramic to metal.

10

#### Example 21

Alloy 214 was etched in  $\text{H}_2\text{SO}_4/\text{HCl}$  for 30 minutes to remove the oxide surface from as-received metal. It was then heat treated in air at  $1200^{\circ}\text{C}$  for 30 minutes. Dielectric composition number 9 was printed with 16 two layers on each side of the metal. This was then followed by dielectric composition 6 printed in one layer on each side. The parts were fired at  $1180^{\circ}\text{C}$  for two minutes in a tube furnace followed by heat treatment at  $900^{\circ}\text{C}$  for 15 minutes in a box furnace.

Thick film Pd/Ag conductors were printed and fired ( $850^{\circ}\text{C}/10$  minutes) on these parts to determine electrical properties of the ceramic dielectric.

20

The parts were then subjected to repetitive thermal shock cycling as per MIL-STD-883C, Method 1011.5B between  $125^{\circ}\text{C}$  and  $-55^{\circ}\text{C}$  liquid heat sinks. Results are set forth in the following Table III.

TABLE III

| Parameter                  | Initial              | After 150 cycles     |
|----------------------------|----------------------|----------------------|
| Resistivity (ohm.cm)       | $7.3 \times 10^{13}$ | $6.9 \times 10^{13}$ |
| Dielectric Constant (1MHz) | 6.5                  | 6.7                  |
| Dissipation Factor (1MHz)  | 0.0060               | 0.0062               |

30

Despite the large TCE difference (metal = 13.3, ceramic = 2.3), no catastrophic failure was detected.

#### Example 22

35 A series of tests were carried out to compare the substrate of Example 21 to alumina with regard to adhesion and conductivity of commercially available hybrid thick film materials applied to the surface of the ceramic using a selection of conductive inks. Although applications for thick film on  $\text{Al}_2\text{O}_3$  are limited due to relatively complex (and costly) packaging schemes needed for mechanical fastening and to protect the fragile alumina from mechanical stress caused by shock, vibration and TCE mismatch,  $\text{Al}_2\text{O}_3$  was selected for evaluation because of its superior electronic properties.

40 Materials from several thick film cast suppliers were printed on the substrate of Example 21 and compared to results on  $\text{Al}_2\text{O}_3$ . The test samples were screened on an MPM TF-100 Printer and fired in a BTU furnace with a standard commercial  $850^{\circ}\text{C}$  profile. The Alumina substrates were Coors 96% material.

45 Adhesion tests were performed on the four metallizations using the procedure described in DuPont technical literature (80 mil (2032 micrometers) squares) using an Instron model 1123. Conductivity of the four metallizations was measured using a 500 Square serpentine pattern 0.010" (254 micrometers) wide.

Results of the study are shown in Table IV.

In the Table IV, the abbreviations have the following meanings:

- (a) "ESL 9633B" is Ag/Pd paste manufactured and sold by ESL Corporation.
- (b) "EMCA C3325" is Ag/Pd paste manufactured and sold by EMCA Corporation.
- (c) "DuPont 9770" is Ag/Pd paste manufactured and sold by Dupont Company.
- (d) "Engelhard A3058" is Ag/Pd paste manufactured and sold by Englehardt Corporation.
- (e) "CCM" is the glass/ceramic coated substrate of Example 21.

55

TABLE IV

| Properties of Thick Film Conductors Fired at 850 ° C for 10 minutes |  |                                |                           |                                |                               |                                |
|---|--|--------------------------------|---------------------------|--------------------------------|-------------------------------|--------------------------------|
| Conductor   | Adhesion (lbs/0.080" square) (kg per 2032 micrometer square) |                                |                           |                                |                               |                                |
|   | Initial  |                                | After 24 hours at 150 ° C |                                | Conductivity (Siemens/Square) |                                |
|   | CCM  | Al <sub>2</sub> O <sub>3</sub> | CCM                       | Al <sub>2</sub> O <sub>3</sub> | CCM                           | Al <sub>2</sub> O <sub>3</sub> |
| ESL 9633B   | 5.4(2.45)  | 5.9(2.68)                      | 4.0(1.82)                 | 4.3(1.85)                      | 11                            | 21                             |
| ECMA C3325  | 4.8(2.18)  | 5.7(2.59)                      | 2.0(0.91)                 | 5.4(2.45)                      | 15                            | 30                             |
| DuPont 9770   | 6.1(2.77)  | 5.9(2.68)                      | 3.0(1.36)                 | 3.0(1.36)                      | 100                           | 200                            |
| Engelhard A3058   | 4.2(1.91)  | 5.5(2.5)                       | 1.4(0.64)                 | 1.7(0.77)                      | 110                           | 170                            |

15 In general, the range of conductivities available on the Example 21 system overlaps quite well with alumina for the materials tested, and any reduced disadvantages attendant to conductivities are more than offset by the superior mechanical properties of the Example 21 substrate.

20 The results of Table IV show that for initial adhesion the adhesion properties of the Comp 2 substrate are comparable to those of alumina. One substrate which was initially comparable to alumina by weakened after aging at 150 ° C. However, the final level achieved was still better than the worst case on alumina with another material.

### Claims

- 25 1. A glass/ceramic coated substrate (10) having a metal core (12) and having on at least a portion of the surface of the metal core a coating (16) of a glass/ceramic comprising (on an oxide basis and based on the total weight of the coatings):
  - from 8 to 26% by weight of magnesium oxide (MgO);
  - from 10% to 49% by weight of aluminum oxide (Al<sub>2</sub>O<sub>3</sub>); and
  - 30 from 42 to 68% by weight of silicon oxide (SiO<sub>2</sub>).
2. A glass/ceramic substrate according to claim 1 wherein said coating comprises cordierite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>).
- 36 3. A glass/ceramic coated substrate according to claim 1 wherein said coating comprises cordierite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) and sapphirine (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>).
4. A glass/ceramic coated substrate according to claim 1 wherein said coating further comprises (on an oxide basis):
  - 40 from 3 to 15% by weight, based on the total weight of MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> in the coating of one or more alkali metal or alkaline earth metal oxides, and a boron oxide.
5. A glass/ceramic coated substrate according to claim 4 wherein said coating comprises cordierite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) and spodumene (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>).
- 45 6. A glass/ceramic coated substrate according to claim 4 wherein said coating comprises cordierite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>), spodumene (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>), and sapphirine (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>), which further comprises (on an oxide basis):
  - 50 from 7 to 9% by weight of one or more alkali metal and/or alkaline earth metal oxides, and boron oxides.
7. A glass/ceramic coated substrate according to claim 1 which further comprises (on an oxide basis)
  - 55 up to 11% by weight based on the total weight of Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and MgO, of a transition metal oxide which functions as a nucleating agent.
8. A glass/ceramic coated substrate according to claim 1 said coating consisting essentially of (on an oxide basis and based on the total weight of the coating):
  - 60 from 9 to 23 weight percent of magnesium oxide;

- (b) from 19 to 50 weight percent of aluminum oxide;
- (c) from 36 to 47 weight percent of silicon dioxide;
- (d) from 1 to 3 weight percent of lithium oxide;
- (e) from 4 to 13 weight percent of a boron oxide; and
- (f) from 0 to 11 weight percent of titanium dioxide or zirconium oxide.

5

9. A glass/ceramic coated circuit board (20) which comprises a metal substrate (12) having coated on at least a portion of the surface thereof a glass/ceramic coating (16) and having defined on at least a portion of the surface of the coating (16) an electrical circuit (18, 22, 24, 26), said coating (16) comprising (on an oxide basis):

- (a) from 8 to 28% by weight of MgO;
- (b) from 10 to 49% by weight of Al<sub>2</sub>O<sub>3</sub>; and
- (c) from 42 to 68% by weight of SiO<sub>2</sub>.

15 10. An electronic substrate (20) comprising:

- (a) a metal substrate (12);
- (b) a glass ceramic (16) comprising (on an oxide basis):

  - (i) from 8 to 26% by weight of MgO;
  - (ii) from 10 to 49% by weight of Al<sub>2</sub>O<sub>3</sub>; and
  - (iii) from 42 to 68% by weight of SiO<sub>2</sub>; and

- (c) a layer (18) of a conductive material, heat bonded and sintered to all or a portion of the surfaces of said glass/ceramic coating (16) in a pre-determined pattern.

#### Revendications

25

1. Substrat revêtu de verre/céramique (10) comportant un noyau de métal (12) et ayant sur au moins une partie de la surface du noyau de métal un revêtement (16) de verre/céramique comprenant (sur la base des oxydes et par rapport au poids total des revêtements) :

  - (a) de 8 à 28 % en poids d'oxyde de magnésium (MgO);
  - (b) de 10 à 49 % en poids d'oxyde d'aluminium (Al<sub>2</sub>O<sub>3</sub>); et
  - (c) de 42 à 68 % en poids d'oxyde de silicium (SiO<sub>2</sub>).

30

2. Substrat verre/céramique selon la revendication 1, dans lequel ce revêtement comprend de la cordiérite (2MgO-2Al<sub>2</sub>O<sub>3</sub>.5SiO<sub>2</sub>).

35

3. Substrat revêtu de verre/céramique selon la revendication 1, dans lequel ce revêtement comprend de la cordiérite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) et de la saphirine (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>).

40

4. Substrat revêtu de verre/céramique selon la revendication 1, dans lequel ce revêtement comprend en outre (sur la base des oxydes) :

  - (d) de 3 à 15 % en poids, par rapport au poids total de MgO, Al<sub>2</sub>O<sub>3</sub> et SiO<sub>2</sub> dans le revêtement, d'un ou plusieurs oxydes de métaux alcalins ou alcalino-terreux, et un oxyde de bore.

45

5. Substrat revêtu de verre/céramique selon la revendication 4, dans lequel ce revêtement comprend de la cordiérite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) et du spodumène (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>).

50

6. Substrat revêtu de verre/céramique selon la revendication 4, dans lequel ce revêtement comprend de la cordiérite (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>), du spodumène (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>), et de la saphirine (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>) qui comprend en outre (sur la base des oxydes) :

  - (d) de 7 à 9 % en poids d'un ou plusieurs oxydes de métaux alcalins ou alcalino-terreux, et des oxydes de bore.

55

7. Substrat revêtu de verre/céramique selon la revendication 1 qui comprend en outre (sur la base des oxydes) :

  - (e) jusqu'à 11 % en poids, par rapport au poids total d'Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> et MgO, d'un oxyde de métal de transition qui fait office d'agent de nucléation.

60

8. Substrat revêtu de verre/céramique selon la revendication 1, ce revêtement étant essentiellement

constitué (sur la base des oxydes et par rapport au poids total du revêtement) :

- (a) de 9 à 23 % en poids d'oxyde de magnésium;
- (b) de 19 à 48 % en poids d'oxyde d'aluminium;
- (c) de 36 à 47 % en poids de dioxyde de silicium;
- 5 (d) de 1 à 3 % en poids d'oxyde de lithium;
- (e) de 4 à 13 % en poids d'un oxyde de bore; et
- (f) de 0 à 11 % en poids de dioxyde de titane ou d'oxyde de zirconium.

9. Plaque (20) pour circuit imprimé revêtue de verre/céramique qui comprend un substrat métallique (12) revêtu sur au moins une partie de sa surface d'un revêtement de verre/céramique (16) et ayant défini sur au moins une partie de la surface du revêtement (16) un circuit électrique (18, 22, 24, 26), ce revêtement (16) comprenant (sur la base des oxydes) :

- (a) de 8 à 26 % en poids de MgO;
- (b) de 10 à 49 % en poids d'Al<sub>2</sub>O<sub>3</sub>; et
- 15 (c) de 42 à 68 % en poids de SiO<sub>2</sub>.

10. Substrat électronique (20) comprenant :

- (a) un substrat métallique (12);
- (b) un verre/céramique (16) comprenant (sur la base des oxydes) :
- 20 (i) de 8 à 26 % en poids de MgO;
- (ii) de 10 à 49 % en poids d'Al<sub>2</sub>O<sub>3</sub>; et
- (iii) de 42 à 68 % en poids de SiO<sub>2</sub>; et
- (c) une couche (18) de matière conductrice, liée et frittée par la chaleur à l'ensemble ou à une partie des surfaces du revêtement en verre/céramique (16) dans une configuration prédéterminée.

25

#### Patentansprüche

1. Glas-/Keramik-beschichtetes Substrat (10) mit einem Metallkern (12) und mit einer Beschichtung (16) aus Glas/Keramik auf zumindest einem Bereich der Oberfläche des Metallkerns, enthaltend (auf einer Oxidbasis und bezogen auf das Gesamtgewicht der Beschichtung):

- (a) von 8 bis 26 Gew.-% Magnesiumoxid (MgO),
- (b) von 10 bis 49 Gew.-% Aluminiumoxid (Al<sub>2</sub>O<sub>3</sub>) und
- (c) von 42 bis 68 Gew.-% Siliciumdioxid (SiO<sub>2</sub>).

2. Glas-/Keramik-beschichtetes Substrat nach Anspruch 1, worin die Beschichtung Cordierit (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) enthält.

3. Glas-/Keramik-beschichtetes Substrat nach Anspruch 1, worin die Beschichtung Cordierit (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) und Saphirin (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>) enthält.

40

4. Glas-/Keramik-beschichtetes Substrat nach Anspruch 1, worin die Beschichtung weiter (auf einer Oxidbasis)

- (d) von 3 bis 15 Gew.-%, bezogen auf das Gesamtgewicht des MgO, Al<sub>2</sub>O<sub>3</sub> und SiO<sub>2</sub> in der Beschichtung, eines oder mehrere Alkalimetall- oder Erdalkalimetalloxide und ein Boroxid

45

enthält.

5. Glas-/Keramik-beschichtetes Substrat nach Anspruch 4, worin die Beschichtung Cordierit (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>) und Spodumen (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>) enthält.

6. Glas-/Keramik-beschichtetes Substrat nach Anspruch 4, worin die Beschichtung Cordierit (2MgO-2Al<sub>2</sub>O<sub>3</sub>-5SiO<sub>2</sub>), Spodumen (Li<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub>) und Saphirin (4MgO-5Al<sub>2</sub>O<sub>3</sub>-2SiO<sub>2</sub>) enthält, welches weiter (auf einer Oxidbasis)

- (d) von 7 bis 9 Gew.-% eines oder mehrere Alkalimetall- und/oder Erdalkalimetalloxide und Boroxide enthält.

55

7. Glas-/Keramik-beschichtetes Substrat nach Anspruch 1, welches weiter (auf einer Oxidbasis)

- (e) bis zu 11 Gew.-%, bezogen auf das Gesamtgewicht des Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> und MgO, eines als Kernbildungsmittel wirkenden Übergangsmetalloxids

enthält.

8. Glas-/Keramik-beschichtetes Substrat nach Anspruch 1, wobei die Beschichtung im wesentlichen aus (auf einer Oxidbasis und bezogen auf das Gesamtgewicht der Beschichtung)

- 5 (a) von 9 bis 23 Gew.-% Magnesiumoxid,
- (b) von 19 bis 48 Gew.-% Aluminiumoxid,
- (c) von 38 bis 47 Gew.-% Siliciumdioxid,
- (d) von 1 bis 3 Gew.-% Lithiumoxid,
- (e) von 4 bis 13 Gew.-% eines Boroxids und
- 10 (f) von 0 bis 11 Gew.-% Titandioxid oder Zirkonoxid

besteht.

9. Glas-/Keramik-beschichtete Schaltplatte bzw. -bild (20), welche ein Metallsubstrat (12) enthält, wobei auf zumindest einem Bereich der Oberfläche eine Glas-/Keramik-Beschichtung (16) aufgebracht ist und 15 wobei auf zumindest einem Bereich der Oberfläche der Beschichtung (16) ein elektrischer Stromkreis (18, 22, 24, 26) definiert ist, wobei die Beschichtung (16) (auf einer Oxidbasis)

- (a) von 8 bis 26 Gew.-% MgO,
- (b) von 10 bis 49 Gew.-% Al<sub>2</sub>O<sub>3</sub> und
- (c) von 42 bis 68 Gew.-% SiO<sub>2</sub>

20 enthält.

10. Elektronisches Substrat (20), enthaltend

- (a) ein Metallsubstrat (12),
- (b) eine Glas-/Keramik-Beschichtung 16, enthaltend (auf einer Oxidbasis)
  - 26 (i) von 8 bis 26 Gew.-% MgO,
  - (ii) von 10 bis 49 Gew.-% Al<sub>2</sub>O<sub>3</sub> und
  - (iii) von 42 bis 68 Gew.-% SiO<sub>2</sub>, und
- (c) eine Schicht (18) eines leitfähigen Materials, welches auf der gesamten oder einem Bereich der Oberfläche der Glas-/Keramik-Beschichtung (16) in einem vorherbestimmten Muster wärmegebunden und gesintert ist.

35

40

45

50

55

FIG. 1

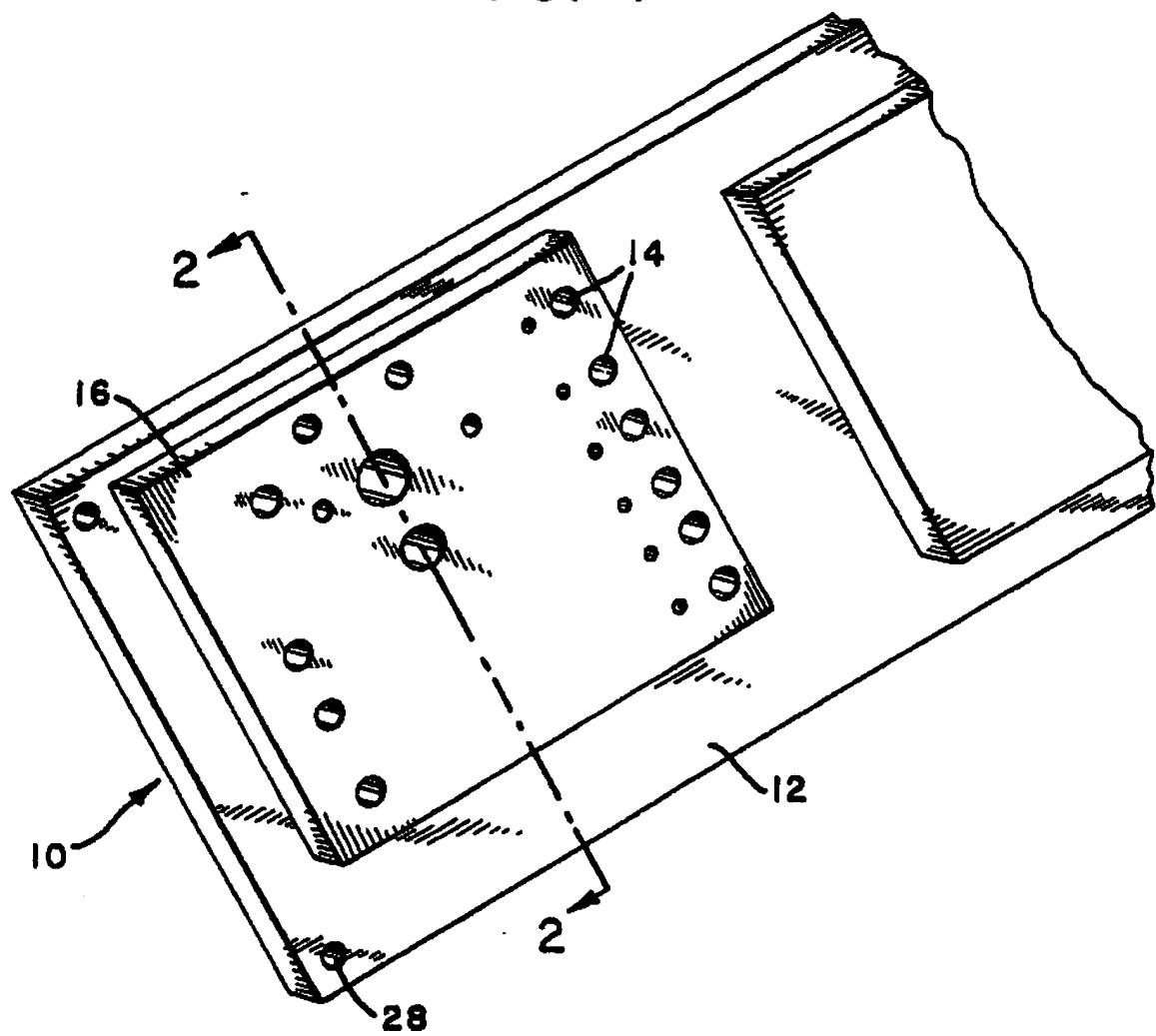


FIG. 2

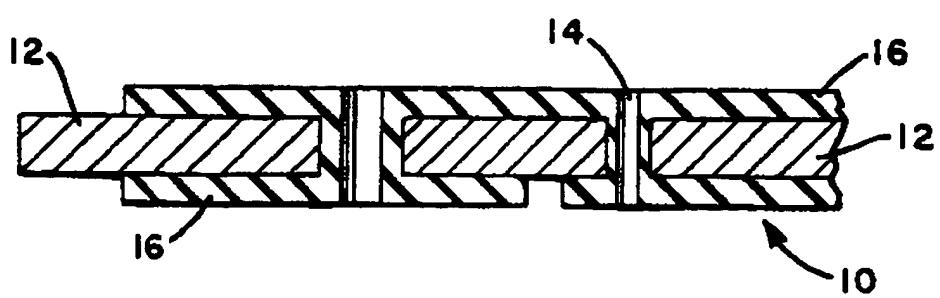


FIG. 3

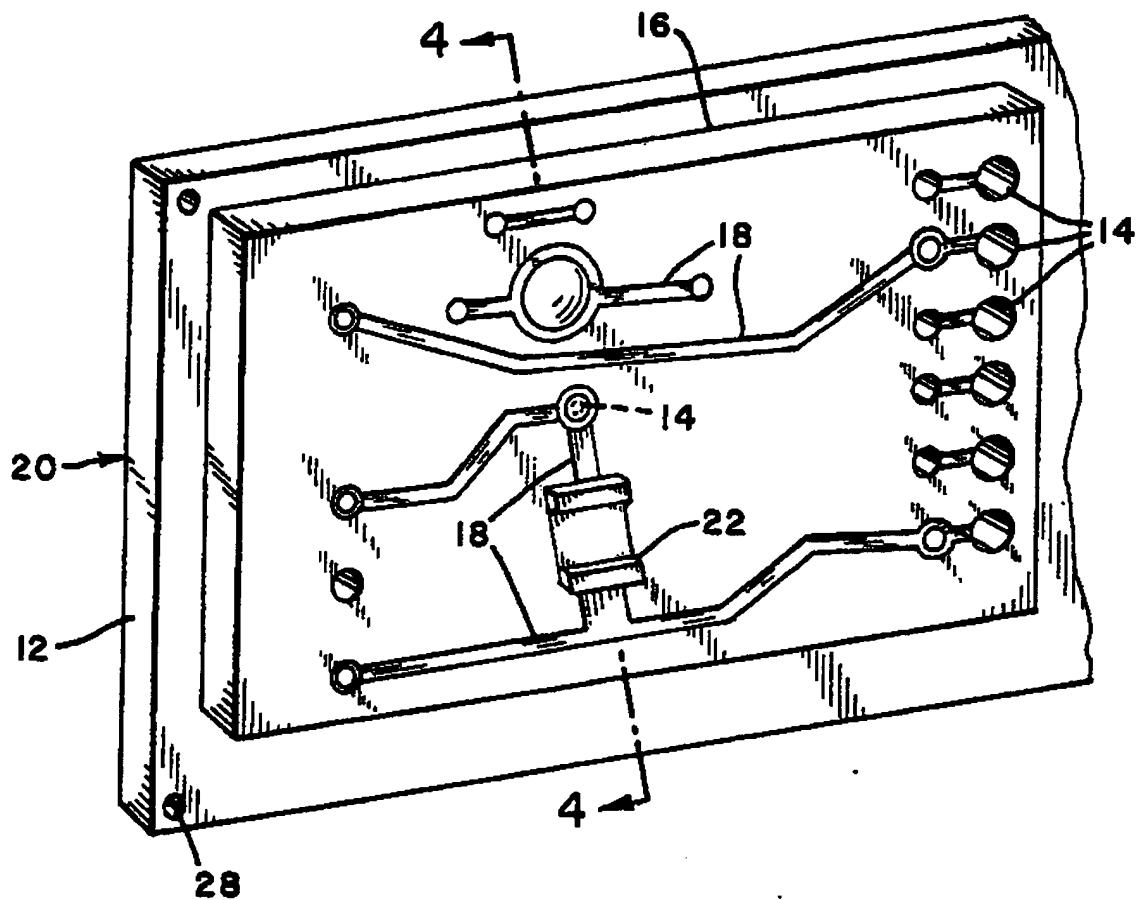
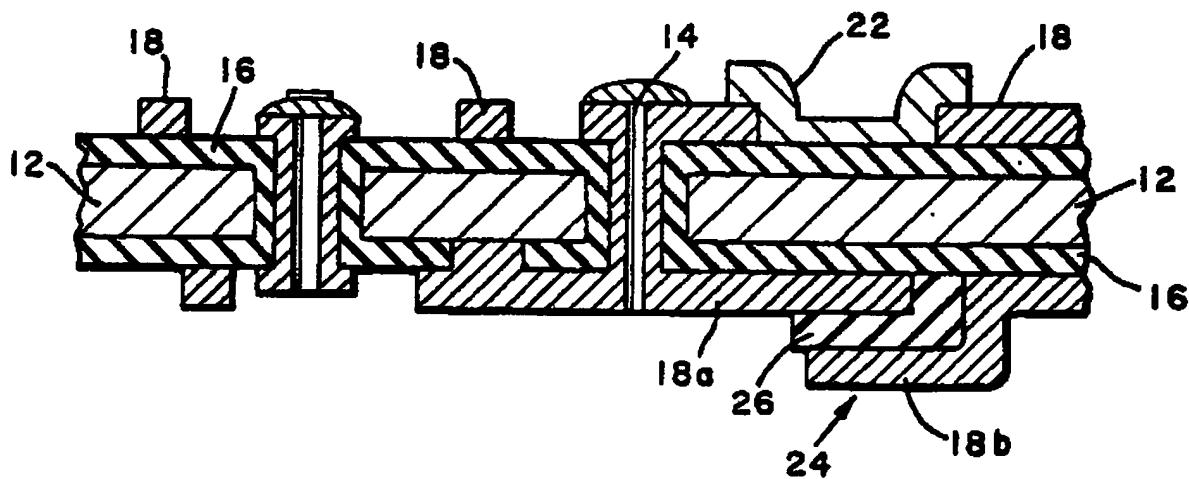


FIG. 4



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

**BLACK BORDERS**

**IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**

**FADED TEXT OR DRAWING**

**BLURRED OR ILLEGIBLE TEXT OR DRAWING**

**SKEWED/SLANTED IMAGES**

**COLOR OR BLACK AND WHITE PHOTOGRAPHS**

**GRAY SCALE DOCUMENTS**

**LINES OR MARKS ON ORIGINAL DOCUMENT**

**REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**

**OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**